Investigation of Rapid Synthesis of Zeolite

A Senior Thesis

Presented in partial fulfillment of the requirements for graduation with research distinction in Chemistry in the undergraduate colleges of The Ohio State University

by

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Abstract

Zeolites are crystalline, microporous aluminosilicates with different pore openings, which with framework T-O-T (T = Si, Al) bonds and channels of molecular dimensions. Crystallization time can be decreased by manipulation and influencing the nucleation and growth characteristic of zeolites. In this study, rapid synthesis of ZSM-5 and Mazzite (Maz) is investigated by manipulating the supersaturation via a dehydration and hydration process. Structural confirmation of the product is obtained by X-ray diffraction (XRD).

The nano size of zeolites make possible unique properties and expands the area of zeolite applications towards, e.g., optoelectronics, chemical sensing, and medicine. However, due to the low yield, complicated synthesis process, and long reaction time, nano zeolites are still not widely used. The rapid crystallization of nanofaujasitic zeolite is investigated by using microwave radiation. The microwave parameters are optimized. Also, the microwave synthesis of nano zeolite Y is studied by using the recycled hydrothermal mother solution. The size of the nanofaujasitic zeolite is characterized by using Dynamic Light Scattering (DLS). Structural conformation of the product is obtained by X-ray diffraction (XRD).

Acknowledgements

I would like to thank my research advisor, Professor Prabir K. Dutta, for the opportunity to conduct research in his laboratory. He has been an inspiring mentor and a person from whom I learned a great deal about conducting research and connecting meaningful thoughts with data. His advice and mentorship throughout the past twosemesters is greatly appreciated, particularly during the graduate school application process.

I thank Mr. Bo Wang, Mr. Chenhu Sun, and the entire Dutta research group for their mentorship, advice, and laboratory instruction.

Finally, I would like to thank my family, whose unconditional and selfless support has made my undergraduate education possible and meaningful. They have offered me far more than I could have ever asked of them.

1. Introduction

ZSM-5 (MFI family of zeolite), which was first reported by Mobil in 1972[1], is a high silica zeolite. Its framework contains of two intersecting channel systems composed of sinusoidal (zigzag) and straight channels with 10-membered ring openings[2]. The framework of ZSM-5 is shown in Figure 1. Mostly the ions located in "alpha" sites can participate in chemical reaction. The "beta" and "gamma" sites inside the pores are inaccessible to reactant. Its unique structure leads to good catalytic activity and shape selectivity. There are several applications in petrochemical processing, fine chemical production, and liquid and gas separation using ZSM-5.

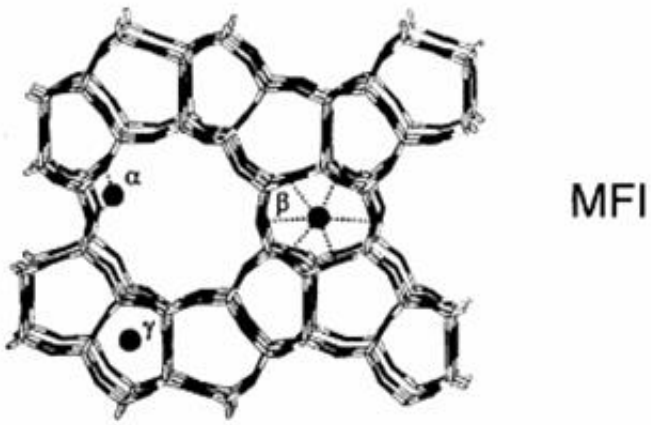

Figure 1. Structure of ZSM-5[3]

Table 1 presents a summary of the literature procedures for ZSM-5 synthesis with varying Si/Al ratios. The time for crystallization varies quite widely, but the fastest synthesis is reported to be 6 hours.

Components	**Condition**	**Reaction time**	**Ref**
60 SiO_2:Al_2O_3:4.5 Na_2O:36 HMI:1198 H_2O	Aged 1h by MW then oven at 175℃	96h	4
40 SiO_2:Al_2O_3:2.4 Na_2O:16 TEA:800 H_2O	Teflon-lined steel autoclaves 170℃	7d	5
50 SiO_2:Al_2O_3:9 Na_2O:14.2 Na_2SO_4:2000 H_2O	After mixing for 30 min autoclave at 170℃	18h	6
51 SiO_2:Al_2O_3:13 Na_2O:2000 H_2O, 7%seeds/SiO_2	Autoclave at 180℃	24h	7
170 SiO_2:Al_2O_3:102 NaCl:17 TPA:3571 H_2O:30 H_2SO_4:33 OH	110℃ 2h then 230℃ for another 4h PH 9.08	6h	8
270 SiO_2:Al_2O_3:78 Na_2O:6.9 $(TEA)_2O$:7550 H_2O	Aged 17h then autoclave at 160℃ for	36h	9

	36h		
32 SiO_2:Al_2O_3:27.4 Na_2O:0.64 TPAOH:305 H_2O	230-260℃, 40-50 atm	10h	10
97 SiO_2:Al_2O_3:14.8 TPAOH:485.4 H_2O	stirred for 5 h at room temperature then 100℃ for 8h, mixture re-crystallized at 140℃	64h	11
100 SiO_2:Al_2O_3:5.6 TPA:3002 H_2O:15 OH	the mixture was stirred at a pH of 10.3 for 1h, then autoclaves at 200℃	7h	12
334 SiO_2:Al_2O_3:95.2 Na_2O:16.7 TPABr:0.17 Fe_2O_3:47 H_2O	autoclave at 150℃, PH 11	24h	13

Table 1. A comparison of ZSM-5 synthesis conditions

Mazzite (MAZ), also an aluminosilicate zeolite is a large pore zeolite whose catalytic properties have been evaluated for gas–oil cracking[14] and hydrocracking[15], aromatic alkylation[16, 17] isomerisation[18], olefin hydration[19], and paraffin isomerisation[20]. MAZ-type zeolites has proven better in some gas phase catalytic reactions than either FAU- or MOR-type zeolites[21, 22].

The framework of mazzite shown in Figure 2 consists of four-ring chains with edge-sharing tetrahedral. The order of the two tetrahedral apices up and one down, which link into a hexagonal structure[23]. There are two types of channels which run parallel to the *c*-axis. One is confined by elliptical eight-membered rings (aperture 5.6 x 3.4 Å), the other by twelve-membered rings of tetrahedra (aperture 7.4 Å). T-O distances are consistent with (Si, Al) disorder[23].

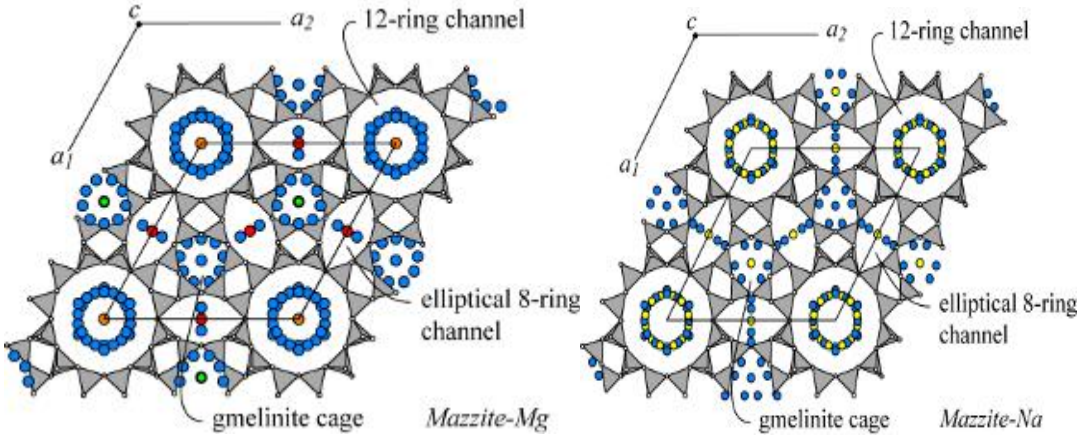

Figure 2. Structure of Mazzite[23]

Table 2 presents a summary of the literature procedures for mazzite synthesis with varying Si/Al ratios. The time for crystallization varies quite widely, but the fastest synthesis is reported to

be 4 days.

Components	**Condition**	**Si/Al**	**Reaction time**	**Ref**
10 SiO_2:Al_2O_3:2.4 Na_2O:0.24 TMA_2O:110 H_2O	Aged for 3 days at room temperature. Crystallization took 10 days at 373 K	25	10d	24
20 SiO_2:Al_2O_3:7NaOH: 5 piperazine:400 H_2O Zeolite Omega	Teflon-lined steel autoclaves 150℃	8.3	4d	25
15 SiO_2:Al_2O_3:5.3 Na_2O:0.3 TMA_2O:270 H_2O	100 ℃		26d	26
15 SiO_2:Al_2O_3:4.8 Na_2O:1.2 TMA_2O:0.1 $NaHPO_4$:240 H_2O	Teflon (PTFE) vessel at 100℃	6	96h	27
67 SiO_2:Al_2O_3:102 NaCl:30 Na_2O: 47 dioxane:1867 H_2O	Autoclave at 140℃	3.4	7d	28

Table 2. A comparison of mazzite synthesis conditions

Here, we report an investigation of rapid synthesis of ZSM-5 and mazzite by manipulating the supersaturation via a dehydration-hydration process. The basic innovation was the use of a novel reactor shown in Figure 3. The aged gel is transferred to the round bottom flask (PTFE, glass) connected to a graduated pressure equalizing addition funnel with a PTFE stopcock topped with a condenser. Therefore, the evaporated water can be collected during the dehydration process.

Fig.3. Novel reactor used in ZSM-5 and MAZ synthesis

Zeolite Y (faujasite family) is widely used as a catalyst, ion exchanging agent and

adsorbent[29-31]. Due to the fact that nanocrystals have high surface areas, fast diffusion characteristics and adjustable porosity, nanofaujasitic zeolite can have many applications such as catalysts, membranes and low-k thin films[32]. For any kinds of applications, a high yield nanocrystal synthesis is needed. However, high nanocrystal yields are usually obtained with longer crystallization time, which results in lager crystal size. In this study, we introduce an economic and rapid method to synthesis nanocrystal zeolite Y using microwave radiation. The mother solution of each batch of reaction can be reused for seven more times, each of which can produce the same yield and size as the first batch. Detailed characterization of the zeolite Y nanocrystals is also presented. This includes powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and dynamic light scattering (DLS).

2. Experimental

2.1 Synthesis of ZSM-5[33]

There are two solutions that need to be prepared. To prepare solution A, 0.45 g of $NaAlO_2$ (0.00175 mole alumina and 0.005 mole NaOH) and 2.95 g of NaOH (0.075 mole) in 25 g distilled water (1.389 mole) is prepared in a 100-mL beaker equipped with a magnetic stirrer. As for solution B, 4.0 g of tetrapropylammonium bromide (0.015 mole) is added to a stirred mixture of 3.1 g of 96% H_2SO_4 and 50 g of distilled water. Solution A and solution B are poured simultaneously into a solution of 30 g of 30% silica solution (0.15 mole SiO_2, 0.0015 mole Na_2O, and 25 g water). The bottle is immediately capped and vigorously shaken to form a gel.

2.2 Synthesis of Mazzite[34]

2.2.1 Seed Preparation

1.0624 g of alumina, 7.0943 g of sodium hydroxide and 15.5626 g of distilled water are

added in a 250 mL of bottom flask. The suspension is refluxed until a clear solution is formed. 29.458g of sodium silicate, 14.0938 g of distilled water and the aluminate solution are mixed in a 200 mL bottle. The mixture is aged for 24 hours at room temperature.

2.2.2 Crystallization Batch Preparation

4.1023 g of alumina, 1.6 g of sodium hydroxide and 14.7267 g of distilled water are added in a 250 mL of bottom flask, and refluxed until a clear solution formed. To prepare solution A, 10 g of tetramethylammonium bromide and 12.5 g of water are mixed together until dissolved. To prepare solution B, 107.3275g of sodium silicate, 3.0796 g of water, 3.465 g of seed solution and solution A are added together sequentially with mixing. The mixture is heated to 80 ℃. To prepare solution C, 12.2918 g of water and 7.7082 g of aluminum sulfate are mixed together until dissolved. Solution B is added to the bottom flask followed by solution C. After the gel is stirred at 80 ℃ for fifteen minutes, the temperature is increased to 100 ℃.

2.3 Microwave synthesis of Nanocrystalline Zeolite Y

2.3.1 Microwave synthesis by using raw gel[35]

To prepare solution A, 26.2 g Ludox HS-30, 10.46 g tetramethylammonium (TMAOH) are measured and added into a Nalgene polypropylene (PP) bottle. To prepare solution B, 76.5 g deionized H_2O, 52.3 g TMAOH, 12.5 g aluminum iso-propoxide (AIP) are measured and added into a dry clean Teflon bottle and the bottle is shaken vigorously. Solution B is put into a water bath at 70 ℃, and stirred until the suspension becomes clear. Then, 11.3 g TMABr was added to the clear solution of aluminum source and kept stirring at room temperature for 15 min. After mixing solution A and B, the mixture is aged for three days at room temperature with stirring. Then, aged gel is moved to microwave tube and heated by microwave for 8 hours at 200W. In

microwave, cooling air flow rate was adjusted to make sure the equilibrated temperature is between 125 and 130 ℃. Product mixture was centrifuged and mother liquor and zeolite product are obtained separately. Mother liquor is reusable and can be recycled. This process can be repeated for seven times with a 70% overall yield.

2.3.2 Microwave synthesis by using mother liquor from hydrothermal synthesis

2.3.2.1 Preparation of Raw gel[35]

For the silicon source, 26.2 g Ludox HS-30 and 10.46 g TMAOH were mixed in a Teflon bottle, sealed with parafilm and stirred at room temperature for 30 min. For alumina source, 12.5 g aluminum isopropoxide was dissolved in 76.5 g H_2O and 52.3 g TMAOH at 70 ℃ hot bath until the suspension became clear. Then, 11.3 g TMABr was added to the clear solution of aluminum source and kept stirring at room temperature for 15 min. Then silicon source and aluminum source were mixed and aged at room temperature with stirring for 3 days.

2.3.2.2 Hydrothermal synthesis

The aged gel was first heated at 100 ℃ in an oil bath with stirring for 4 days. After that, product mixture was centrifuged and mother liquor and zeolite product are obtained separately.

2.3.2.3 Microwave synthesis with mother liquor

21 ml of mother liquor from hydrothermal synthesis and 0.015 g NaOH are mixed together and put into a microwave tube. The mixture is heated for 1 hour at 300W. In microwave, cooling air flow rate was adjusted to make sure the equilibrated temperature is 135 ℃. After microwave heating, the product mixture was purified with low-speed centrifuge to remove large particles, if any. After purification with low-speed centrifuge, product mixture was centrifuged with ultracentrifuge to capture nano zeolite particles from its mother liquor. Isolated nano zeolite

particles were washed by repeating the centrifuge step and sonication process until pH 7. After that, nano zeolite was stored as a 1 wt% dispersion.

2.4 Characterization

Diffraction patterns were collected by using a Bruker D8 Advance with Ni filtered Cu K_a radiation using a 1s dwell time and 0.1^0 step size. High-resolution scanning electron micrographs were collected using a Sirion FEG SEM which equipped with high-resolution field emission guns. Measurements were made on washed, gold-coated samples. DLS measurements were made using dilute aqueous colloidal suspensions of synthesis products. Sample temperature was controlled at room temperature via fluid circulation through the jacket.

When atoms are in different arrangements, they have different crystal structures and different planes atoms which lead to different diffraction patterns. Powder x-ray diffraction can exam many randomly oriented crystals with alignment of just a few of them being appropriate for the x-ray beam set up. A fine homogeneous powder is packed into a sample holder. X-ray tube is made of a highly evacuated tube with a tungsten filament cathode and a large anode consisting of copper. The output of this test is a two dimensional figure of peaks representing different lattice planes. The schematic diagram powder of x-ray diffraction is shown in figure 4.

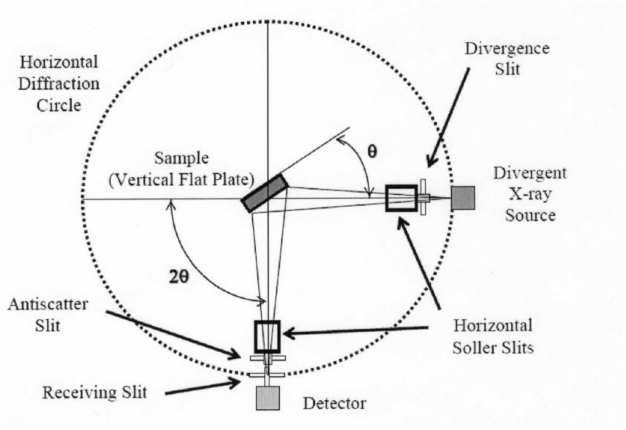

Figure.4. Powder X-ray Diffractometer[36]

Scanning electron microscope (SEM) is a type of electron microscope. Images of a sample can be produced by being scanned with a focused beam of electrons. The electrons can interact with atoms in the sample which can produce different signals about the sample's surface topography and composition. The electron beam is emitted by an electron gun fitted with a tungsten filament cathode. The electron beam interacts with the sample. And the electrons lose energy by repeated random scattering and absorption. The energy change between the sample and electron beam lead to the emission of secondary electrons by inelastic scattering, the reflection of high-energy electrons by elastic scattering, and the emission of electromagnetic radiation. Each of them can be detected by the detector. The schematic diagram of scanning electron microscope is shown in figure 5

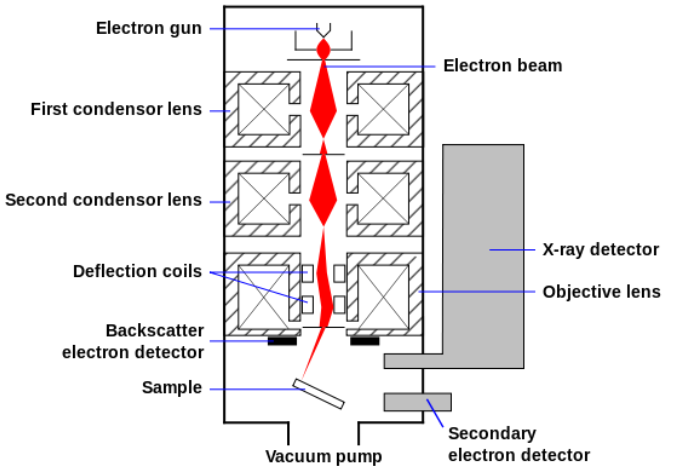

Figure.5. Scanning electron microscope [37]

Usually the light source of dynamic light scattering is a leaser which is monochromatic and coherent. When molecules in the solution are hit with the light, all of the molecules diffract the light in all directions. The diffracted light can be interfering constructively or destructively. The resulting set of speckle patterns produced by the repeated process in short time intervals are analyzed by an autocorrelator. When small particles are hit by the source light, the scattering

intensity fluctuates over time. This fluctuation is because of the Brownian motion of small molecules in solution. Therefore, the distance between the scatterers in the solution is constantly changing with time. Hypothetical dynamic light scattering of large and small particles are shown in figure 6.

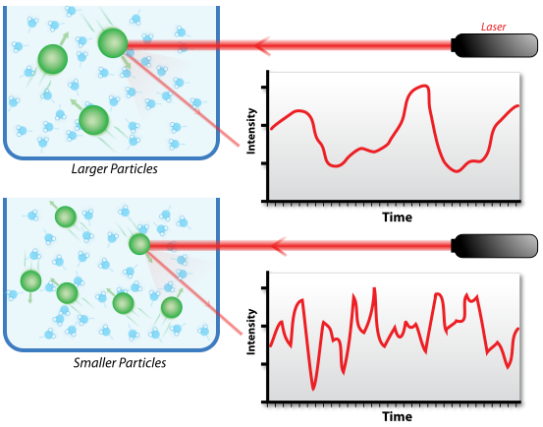

Fig.6. Hypothetical dynamic light scattering of large and small particles[38]

3. Results and discussion

3.1 Rapid synthesis of ZSM-5

The control experiment was done with the conditions described in the experimental section. The X-ray diffraction patterns (XRD) are shown below in Figure 7. Compared with the XRD pattern in Figure 8, the full crystallization time is around 81h.

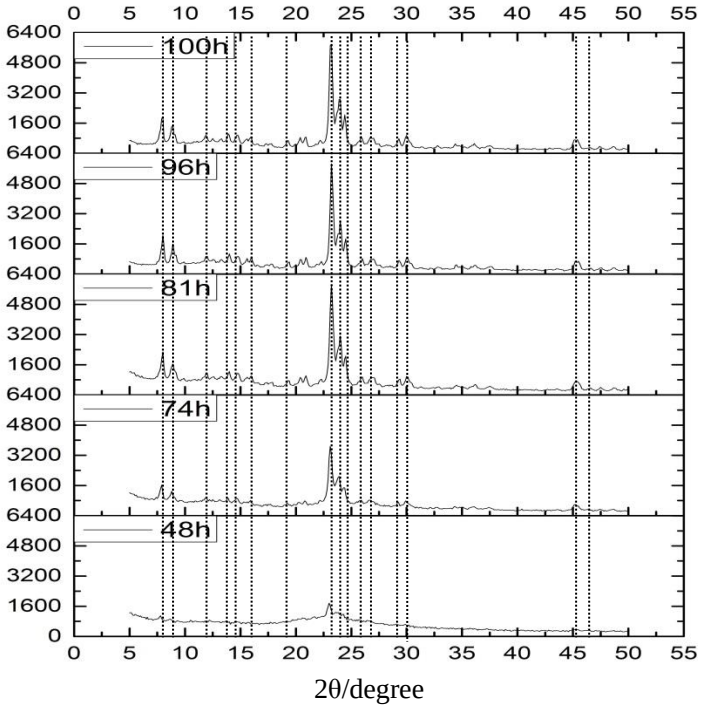

Fig.7. XRD patterns of ZSM-5 for control experiment

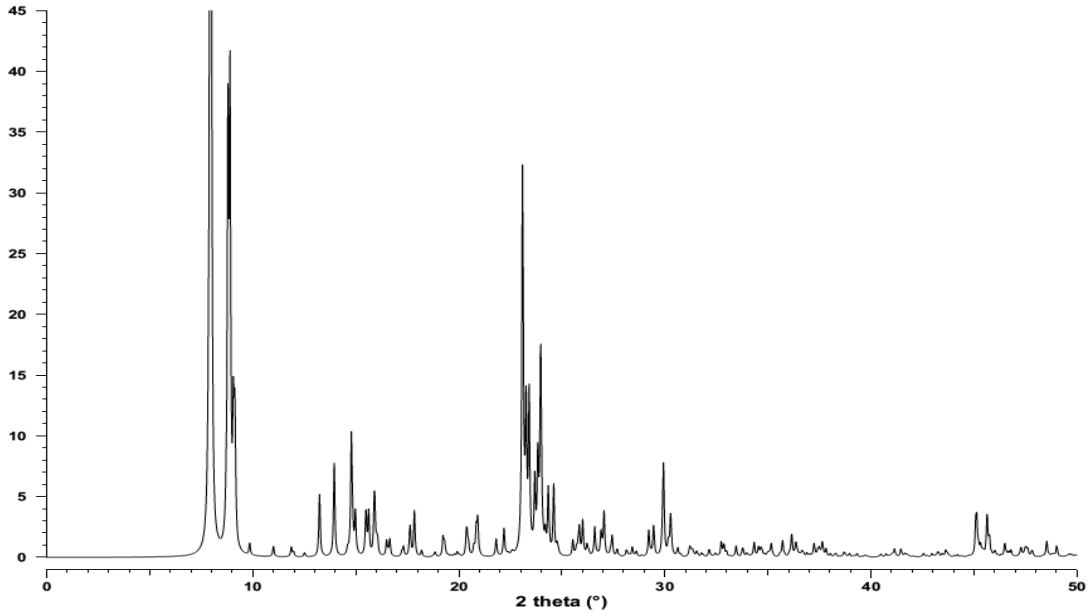

Fig.8. XRD patterns of ZSM-5, Calcined[39]

The following experiments focus on trying to speed up the crystallization process. The strategy taken was similar to the procedure we have reported for FAU zeolites[40]. The basic

innovation was the use of a novel reactor shown in Figure 3. The aged gel is transferred to the round bottom flask (PTFE, glass) connected to a graduated pressure equalizing addition funnel with a PTFE stopcock topped with a condenser. Only the reflux part of the apparatus can be used (temperature of reflux is 100-103 ^{o}C). Also, while under reflux, H_2O from the reaction can be removed by condensation in the addition funnel over a period of time, and the reflux can be continued. The collected water can also be re-added back dropwise to the concentrated gel over a period of time, along with other reagents to speed up the crystallization. As detailed below, several methods were examined.

Method	Numbers of cycle	Water extraction amount (mL)	Total concentrated gel reaction time (h)	Crystalization time (h)
Method I	10	15	5	73
Method II	9	15	29	53
Method III	1	15	24	69
Method IV	1	30	24	57
Method V	1	30	30	51

Table 3. Overview of ZSM-5 synthesis methods

Method I

The reaction was continued under reflux for two hours. Then, evaporated water was collected by the constant pressure drop funnel for fifteen minutes. 15 mL of water was collected (15 % of the water). After thirty minutes' reaction, water was dropped back in fifteen minutes. The solution continued to react for thirty minutes. The same procedure was repeated for ten times. Timeline is shown in Figure 8.

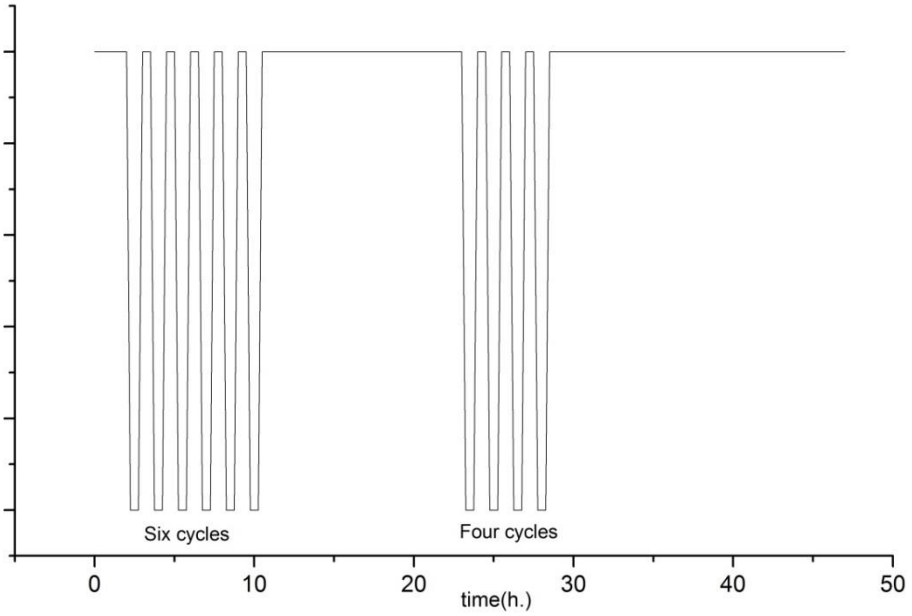

Fig.9. Timeline of reaction for Method I

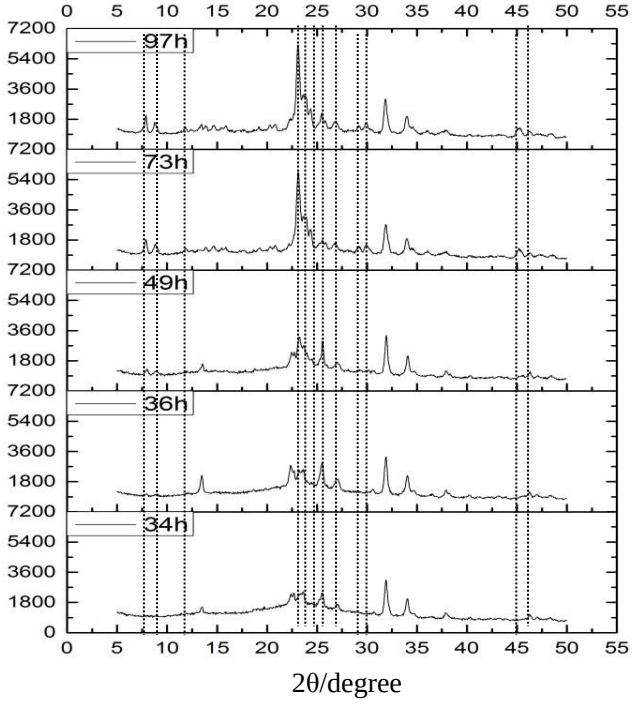

Fig.10. XRD patterns for Method I

The XRD pattern, which is shown in Fig. 9, demonstrates that the crystallization time is around 73h. Compared with the control experiment, the crystallization time of this method is shorted by about 7 hours. The time for complete crystallization is slightly decreased which means that the

dehydration-hydration process can help reduce crystallization time. Therefore, in the next method concentrated gel is reacted for longer time.

Method II

The reaction was continued under reflux for two hours. Then, evaporated water was collected by the constant pressure drop funnel for fifteen minutes. 15 mL of water was collected (15 % of the water). After thirty minutes' reaction, water was dropped back in fifteen minutes. The solution continued to react for thirty minutes. The same procedure was repeated nine times. After the first five and last four cycles, evaporated water was extracted. The concentrated gel continued to react for twelve hours each. Then water was dropped back after 43 hours' reaction time. Timeline is shown in Figure 10.

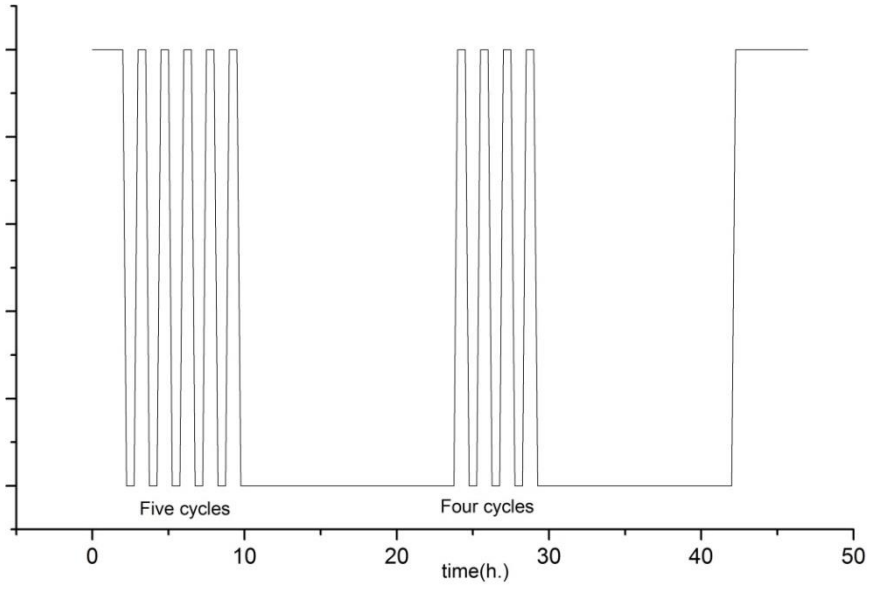

Fig.11. Timeline of reaction for Method II

The XRD pattern, which is shown in Fig. 11, demonstrates that the crystallization time is between 51-53h. Compared with the control experiment, the crystallization time of this method is shorter by about thirty hours. However, the synthesis process is still very complicated which is not practical for mass production in industry. Therefore, in next method nine cycles are reduced to one

cycle.

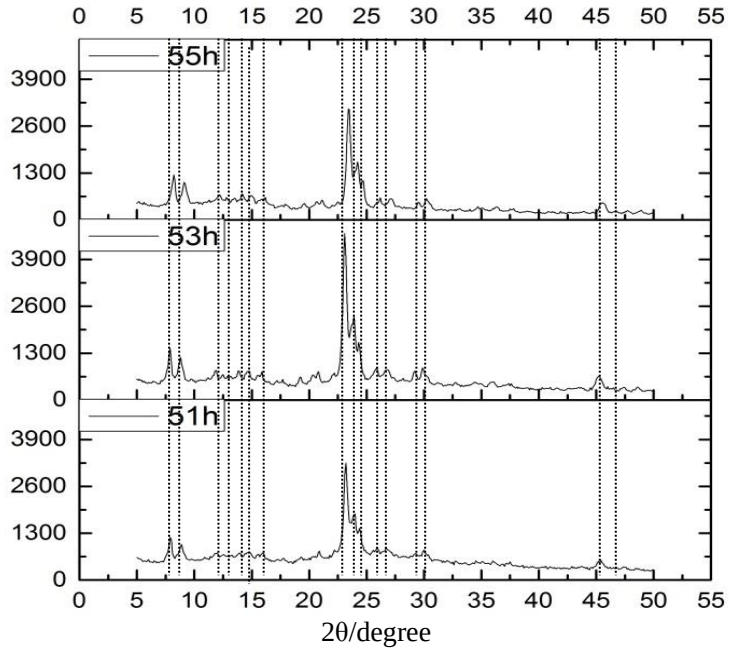

Fig.12. XRD patterns for Method II

Method III

The reaction was under reflux continued for six hours. Then, evaporated water was collected by the constant pressure drop funnel for fifteen minutes. 15 mL of water was collected (15 % of the water). After twenty four hours' reaction, water was dropped back in fifteen minutes. Timeline is shown in Figure 12.

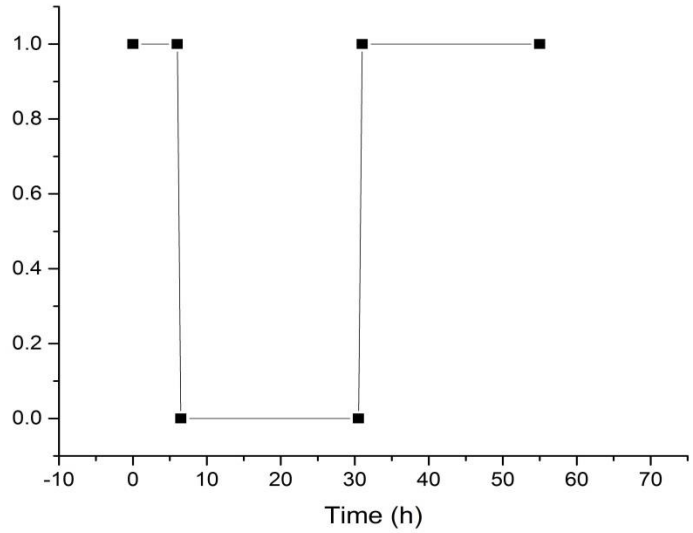

Fig.13. Timeline of reaction for Method III

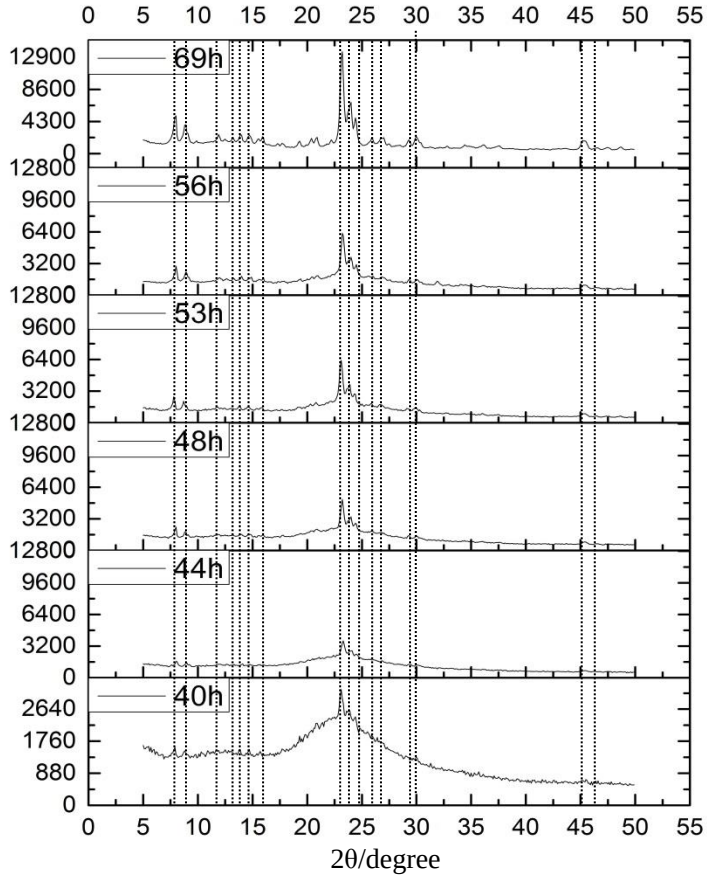

Fig.14. XRD patterns for Method III

Compared with method II, the XRD pattern, which is shown in Fig.13, demonstrates that the mixture is not fully crystalized at 56h. According to Tompson and his coworker's work[41,42], this suggests that the increasing supersaturation is a possible reason for the increase in the nucleation rate. Therefore, for next method, more water was collected to produce a more concentrated gel.

Method IV

The procedure of this method is exactly the same with method III except that 30 mL of evaporated water is collected by the constant pressure drop funnel**.** The XRD pattern, which is shown in Fig. 14, demonstrates that the fully crystallization time is around 57h. Compared with method III, the crystallization time of this method is shorter. This method supports the hypothesis that increasing supersaturation can increase nucleation rate. However, the result of this method is still not as good as method II. Therefore, the process needs further optimization.

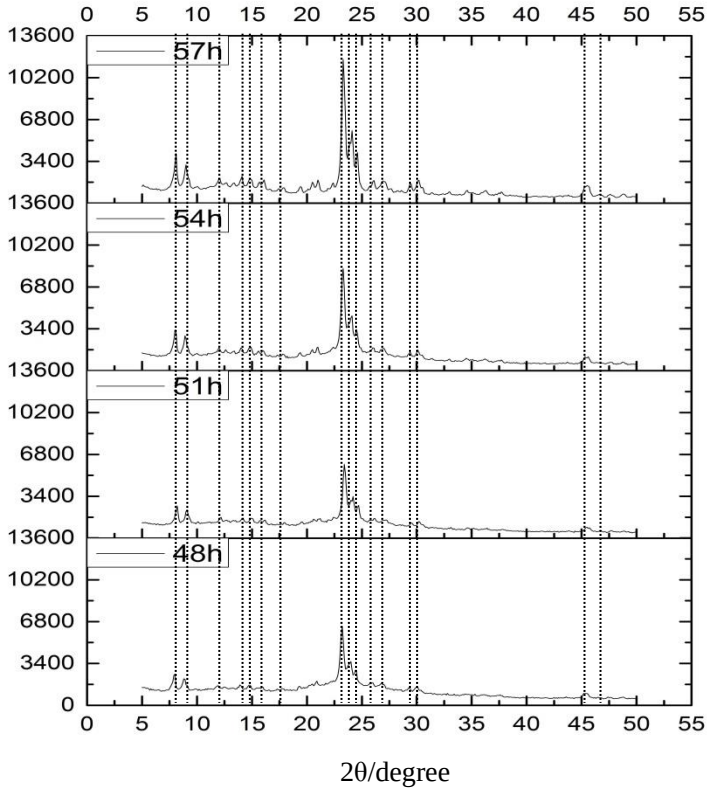

Fig.15. XRD patterns for Method IV

Method V

The reaction was continued under reflux for six hours. Then, evaporated water was collected by the constant pressure drop funnel for one hour. 30 mL of water was collected (30 % of the water). After thirty hours' reaction, water was dropped back in one hour. Timeline is shown in Figure 15.

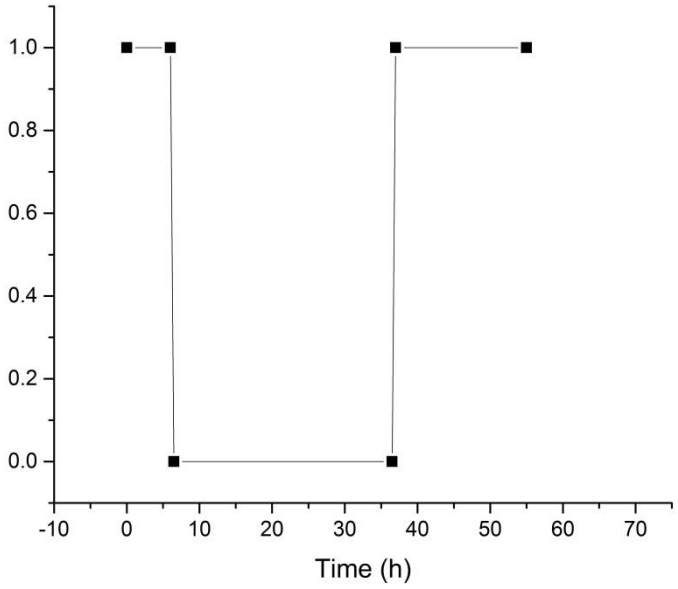

Fig.16. Timeline of reaction for Method V

The XRD pattern, which is shown in Fig. 16, demonstrates that the crystallization time is around 51h. Compared with the control experiment, the crystallization time of this method is shorter by about thirty hours. This method verifies that longer reaction time of concentrated gel can increase nucleation rate. This method has a simpler process than method II with a similar result. However, more investigations should be done for further optimization.

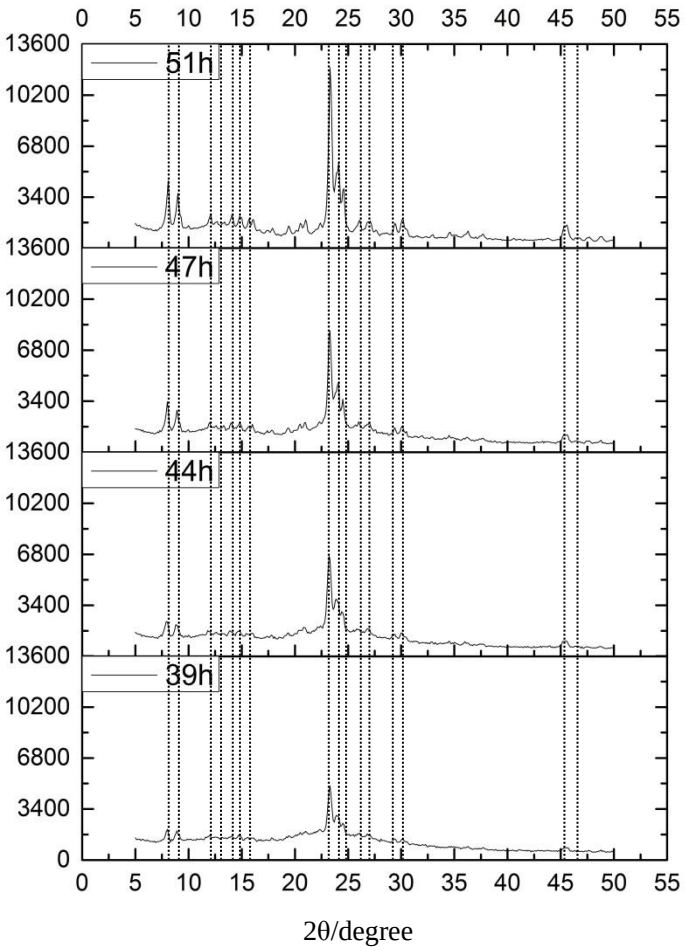

Fig.17. XRD patterns for Method IV

The mechanism has been studied for years. In the report of Edith Flanigen and Donald Breck[43], the nucleation and growth of zeolite crystals from the reaction mixture are illustrated. The S-shaped growth curves are described which is shown in figure 17. There is a long induction time (nucleation time) followed by a sudden rapid growth.

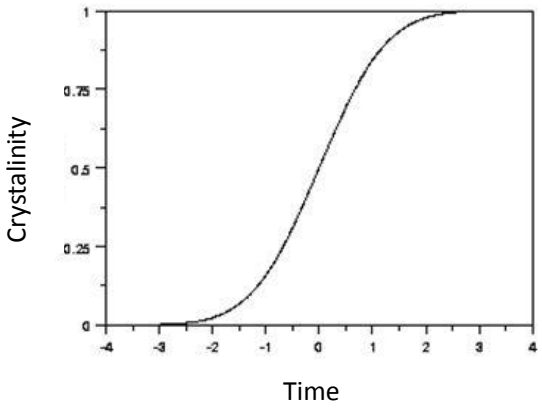

Fig.18. S-shaped growth curve

Chang and Bell[44] have summarized nucleation of zeolites as following steps : (a) formation of clathrate-like water structure around the template,(b) isomorphous substitution of silicate for water in these cages (which resemble ZSM-5 channel intersections), and (c) progressive ordering of these entities into the final crystal structure. Mechanism of crystal growth is shown in figure 18. Also, major changes in gel structure occur during the early stages of reaction. In the tetrapropylammonium (TPA) system, embryonic structures are formed rapidly upon heating. This is the reason that why we continued the reaction under reflux for six hours before the dehydration process. The crystallization of ZSM-5 also shares the S-shaped growth curve. We mainly affect the step b and c by manipulating the supersaturation via a dehydration and hydration process. When water is taken out of the gel, it helps the substitution of silicate for water. After water is dropped back, the excess water can help to transport the nutrients to form ordering final crystal structure.

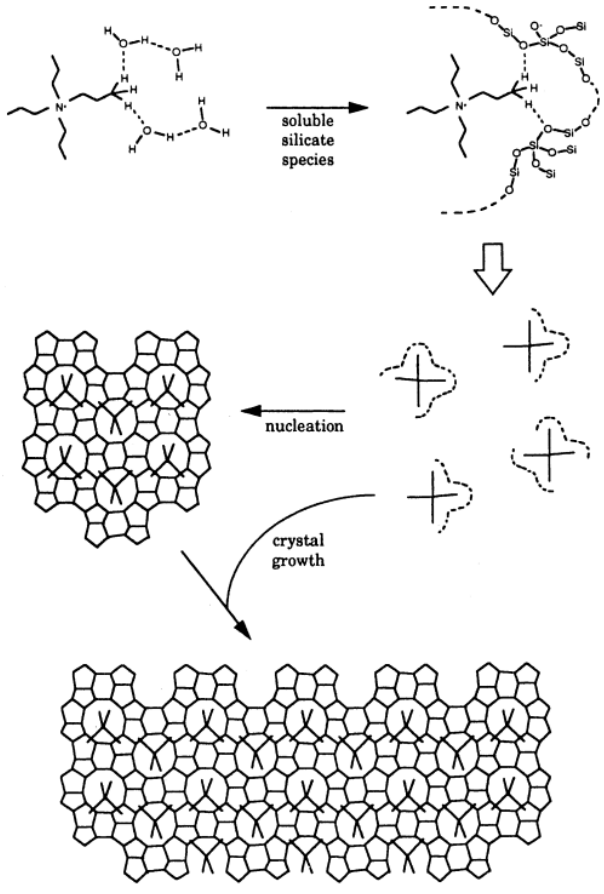

Fig.19. Mechanism of crystal growth of ZSM-5[44]

3.2 Rapid synthesis of Mazzite

The control experiment was done with the conditions reported in experimental section. The

X-ray diffraction patterns (XRD) are shown below in Figure 19. According to the XRD pattern, the crystallization time is between 36-42h.

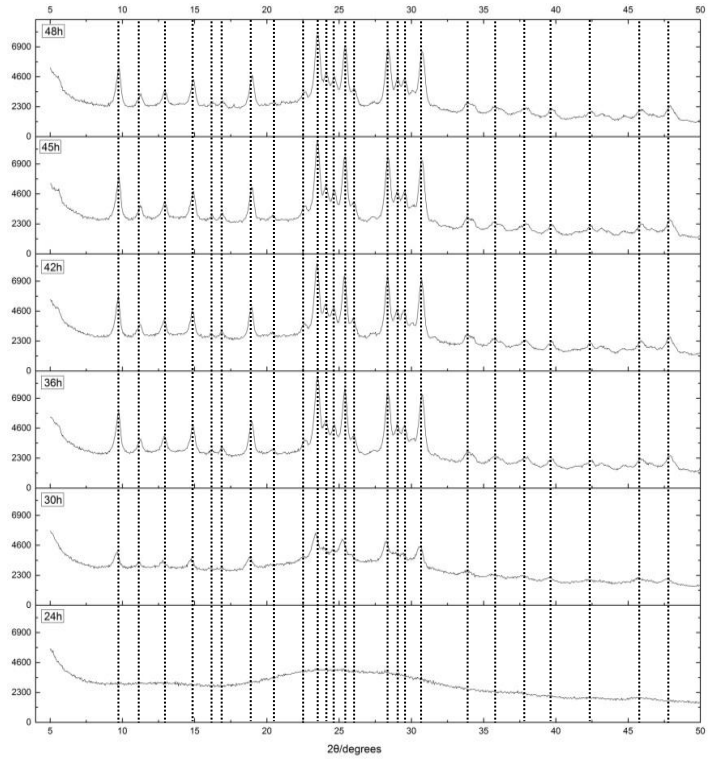

Fig.20. XRD patterns of Mazzite for control experiment

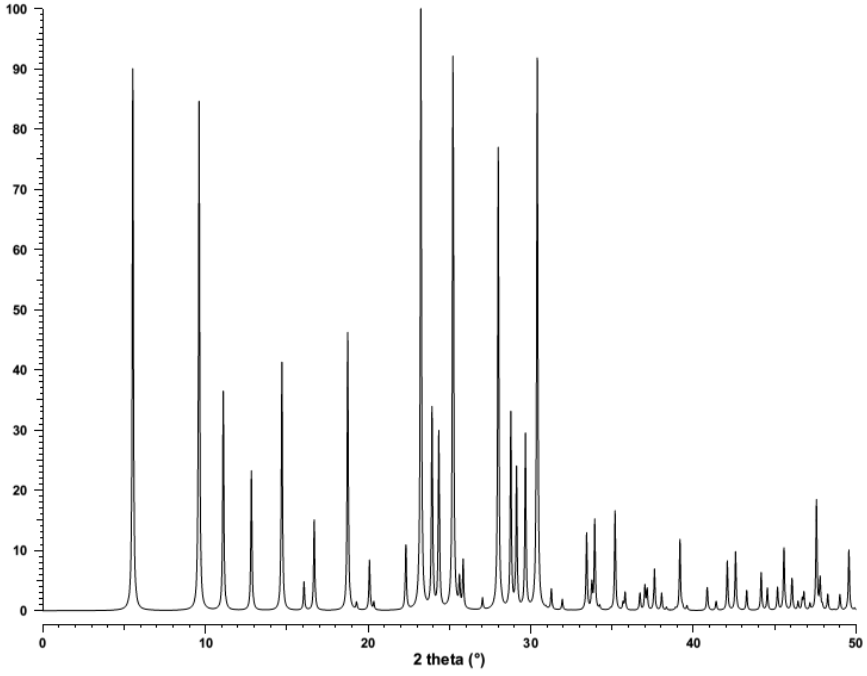

Fig.21. XRD patterns of mazzite, Calcined[45]

The following experiments focus on trying to speed up the crystallization process. The strategy taken was similar to the procedure we carried out for ZSM-5 synthesis. The basic innovation was the use of the novel reactor shown in Figure 3. And the strategies is similar with ZSM-5 synthesis

Method	Numbers of cycle	Water extraction amount (mL)	Total concentrated gel reaction time (h)	Amount of p-dioxane (mL)
Method I	6	11	3	6
Method II	6	20	3	6
Method III	6	20	3	6
Method IV	6	20	3	6
Method V	6	20	3	6

Table 4. Overview of mazzite synthesis methods

Method I

The reaction was continued under reflux for two hours. Then, evaporated water was collected by the constant pressure drop funnel for fifteen minutes. 11 mL of water was collected (8 % of the water). After thirty minutes' reaction, water was dropped back in fifteen minutes. The solution continued to react for thirty minutes. The same procedure was repeated six times. Timeline is shown in Figure 20.

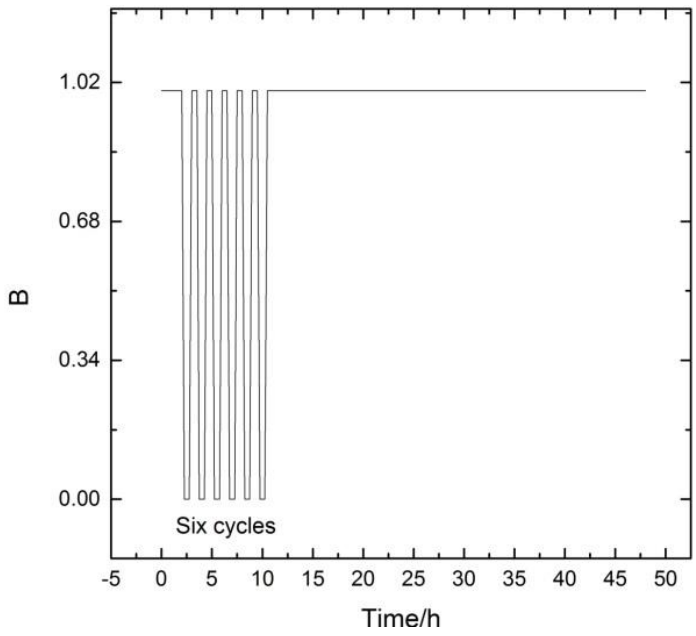

Fig.22. Timeline of reaction for Method I

The XRD pattern, which is shown in Fig. 21, demonstrates that the crystallization time is between 27- 30h. Compared with the control experiment, this method is shorter by about 6-20 hours.

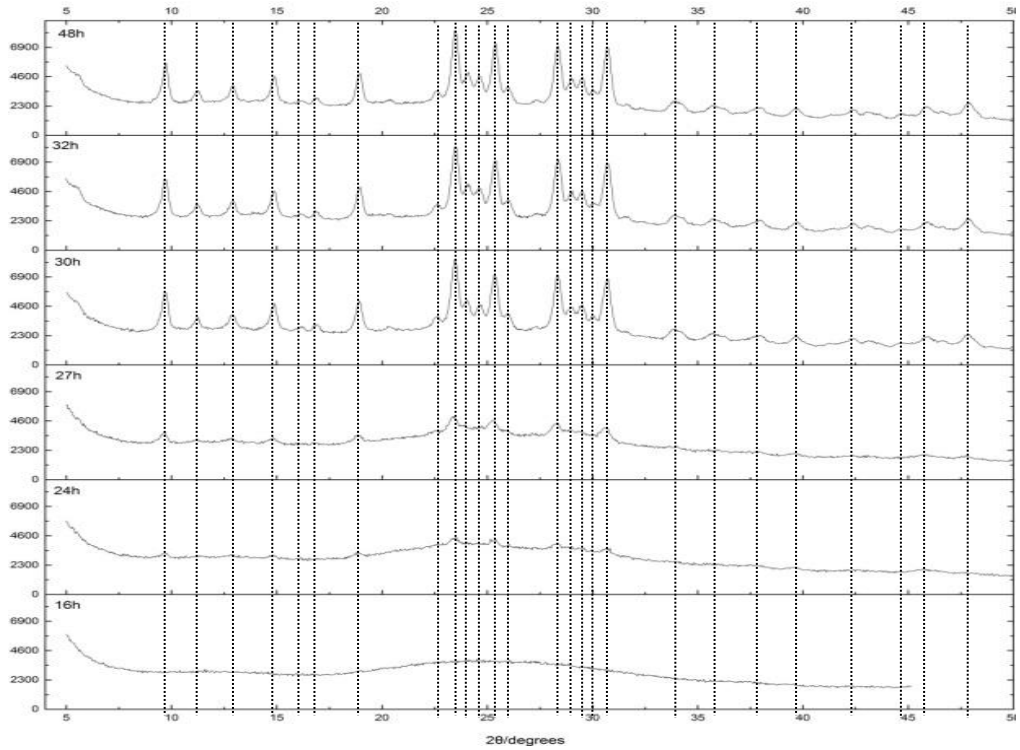

Fig.23. XRD patterns for Method I

Method II

As for the second method, the reaction was continued under reflux for two hours. Then, evaporated water was collected by the constant pressure drop funnel for thirty minutes. 20 mL of water (14% of the total water) was collected. After thirty minutes' reaction, water was dropped back in thirty minutes. The solution continued to react for thirty minutes. The same procedure was repeated for six times. Timeline is shown in Fig.22.

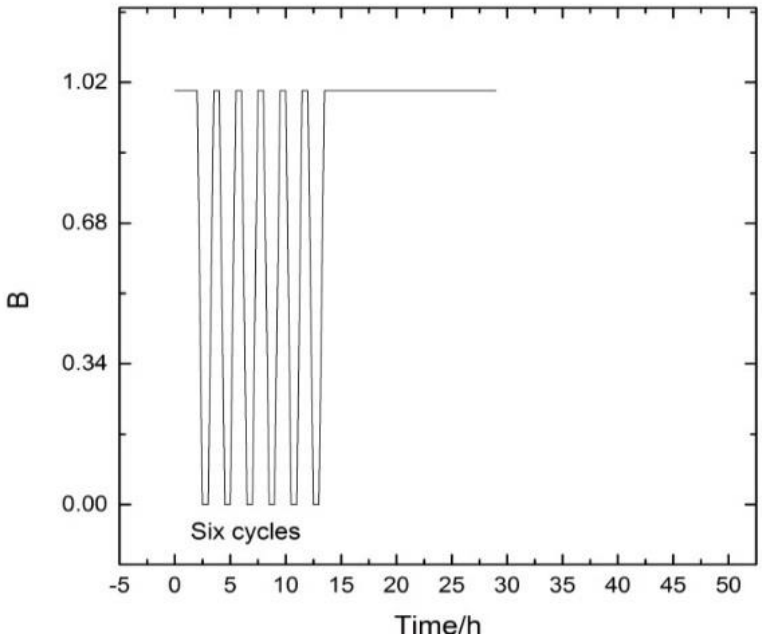

Fig.24. Timeline of reaction for Method II

The XRD pattern, which is shown below in Figure 23, demonstrates that the fully crystallized product is obtained faster than Method I in 29h, but it is a mixture of sodalite (*) and mazzite.

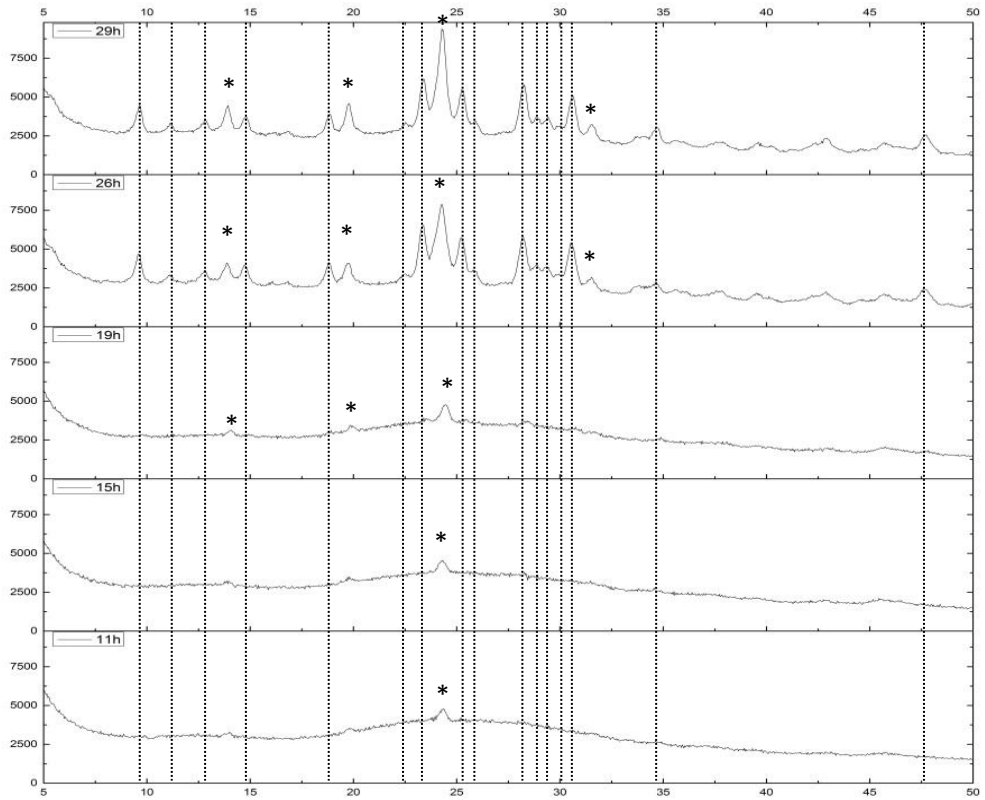

Fig.25. XRD patterns for Method II

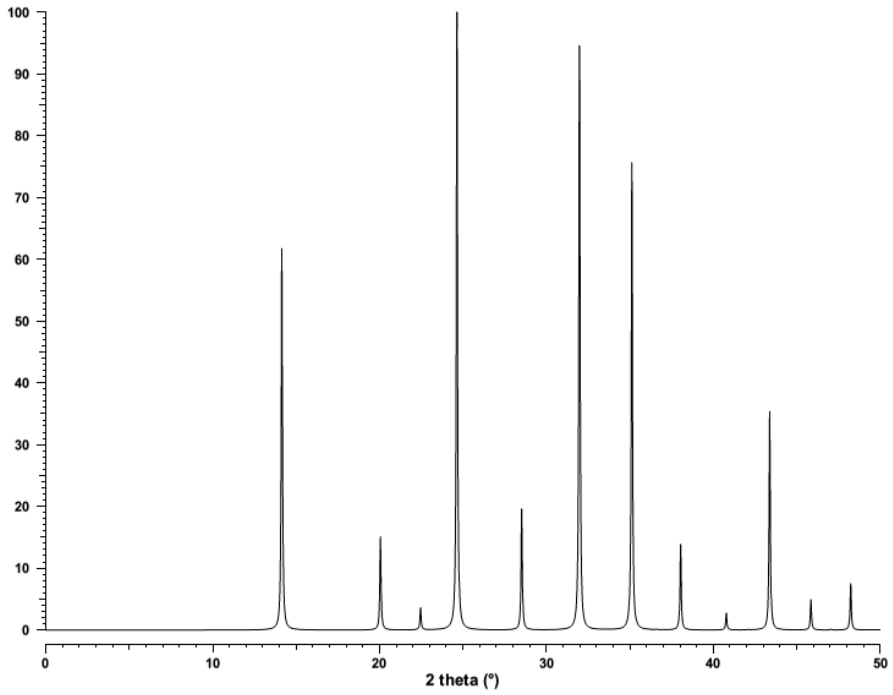

Fig.26. XRD patterns of sodalite, Calcined[46]

Thus, next effort was focused on minimizing the amount of SOD. It has been identified that tetramethyl ammonium (TMA^+) exhibits good structure directing capability both for gmelinite

and sodalite cages[47].In Method II, it looks like the crystallization of sodalite is preferred in the concentrated gel with high alkalinity. It is reported that the crystallization of mazzite is promoted with p-dioxane[48]. We tested the hypothesis that in the concentrated gel, a high alkalinity and low dioxane mixture will promote the selectivity of mazzite. It is possible that addition of small amount of p-dioxane can not only retard the formation of sodalite but also increase the rate of mazzite. . Anything more than 6 mL of dioxane leads to aggregation of the gel, and so addition of p-dioxane was kept below this limit. Three new methods were tried.

Method III

The procedure of cycles is the same with previous two methods except that 1 mL of p-dioxane is added with the water at each cycle. The XRD pattern, which is shown below in Figure 24, shows that the product is still a mixture of mazzite and sodalite. Also, the p-dioxane seemed to hamper both crystallization of mazzite and sodalite.

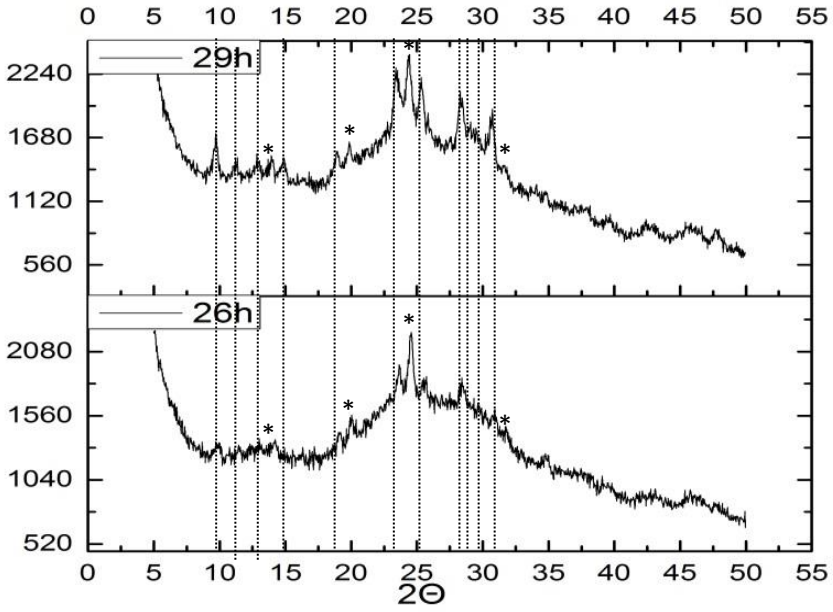

Fig.27. XRD patterns for Method III

Method IV

As for method four, the procedure of cycles are the same with previous experiments except that 2 mL of p-dioxane each was added into the water which is extracted out in the first three cycles. It can be observed that the mixture began to crystalize at 22 hours which is earlier than method III. Therefore, it can be conjectured that more dioxane can increase the rate of crystallization. The XRD pattern is shown below in Figure 25.

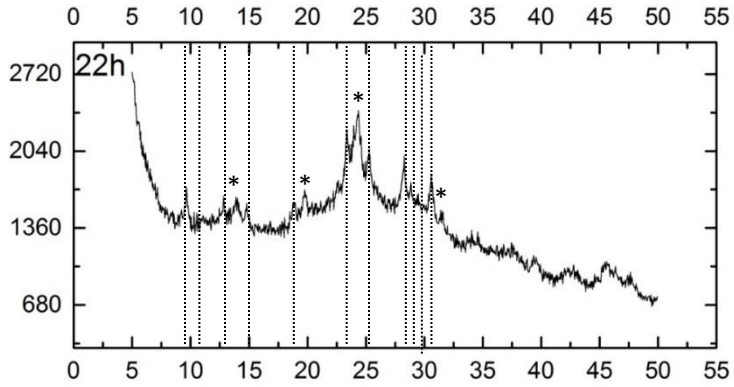

Fig.28. XRD patterns for Method IV

Method V

As for method V, the number of cycles is the same with previous experiments except that 0.5 mL of p-dioxane is added into the gel right after the water is taken out and 0.5 mL is then added back to the gel with water for each cycle. The XRD pattern is shown below in Figure 26.

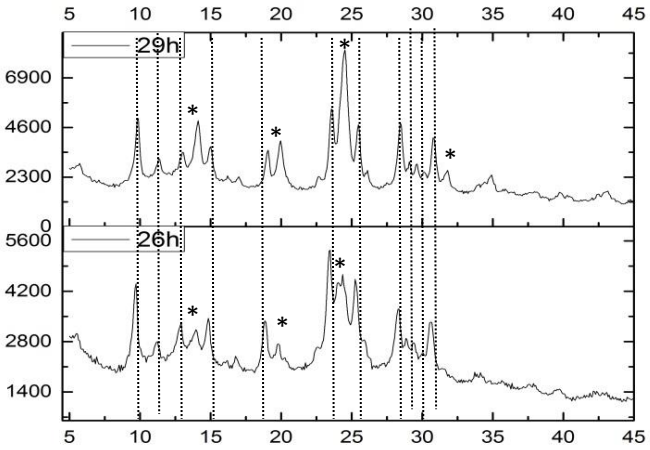

Fig.29. XRD patterns for Method V

It can be observed from the XRD pattern that the crystallization of mazzite began earlier than sodalite. Compared with method III and IV, this means that dioxane can hamper the formation of sodalite. In method two and three, dioxane added into the gel can also be collected by the constant pressure drop funnel because of the similar boiling point with water. There may be not enough dioxane in the concentrated gel. We are concluding that increasing the amount of dioxane in concentrated gel will hamper the formation of sodalite, and speed up formation of mazzite.

The mechanism of crystallization of mazzite is similar with ZSM-5. However, tetramethyl ammonium (TMA^+) exhibits good structure directing capability both for gmelinite and sodalite cages. Therefore, there is a competitive process between the formation of sodalite and gmelinite cages. When the gel is under normal condition, sodalite cage formation is hampered. However, the high alkalinity condition produced by the dehydration process leads to the formation of both sodilate and gmelinite. The addition of p-dioxane affects the step a of the nucleation process as mentioned in ZSM-5. Because of the different abilities of TMA^+ and p-dioxane to complex cations[49], the formation of clathrate-like water structure of sodalite around the template is

hampered. This may explain why the formation of sodalite is retarded with the addition of p-dioxane in method V.

3.3 Microwave synthesis of Nanofaujasitic Zeolite

Table 3 summarizes the results from several experiments designed to optimize the microwave parameters. Lower microwave power takes longer crystallization time. But, lower microwave power yields higher portion of nano zeolite particles in product mixture and the size of nano particles are smaller. As listed in the table 3, the optimal parameters for microwave synthesis takes eight hours with 200 W for fully crystalized nanofaujastic zeolite with relatively high yield. The product is a mixture of large and small particles. The nanofaujasitic zeolite needs to be purified with low speed centrifuge. XRD patterns of these batches with centrifuging are shown in Figure 27-30. Batch 5 takes less time for complete crystallization with high yield. Compared with hydrothermal synthesis that takes 96 hours for crystallization, microwave synthesis decreases the crystallization time to 8 hours which is twelve times faster. SEM image of the fifth batch of nanofaujasitic zeolite is shown in Fig. 31.

Batch	MW condition	DLS/nm	Yield %	Comments
1	180W8h	84	4	Not fully crystalized
2	180W10h	79	7	Not fully crystalized
3	180W12h	65	6.9	Fully crystalized
4	200W6h	95	4.2	Not fully crystalized
5	200W8h	65	7	Fully crystalized
6	200W10h	65	7.1	Fully crystalized
7	250W4h	81	5	Small zeolite Y is not small enough
8	250W6h	73	2	More large particles
9	300W3h	96	2	Less of both large and small particles
10	300W4h	97	3.5	Small zeolite Y is not small enough

Table 5. Microwave Synthesis of nano zeolite Y

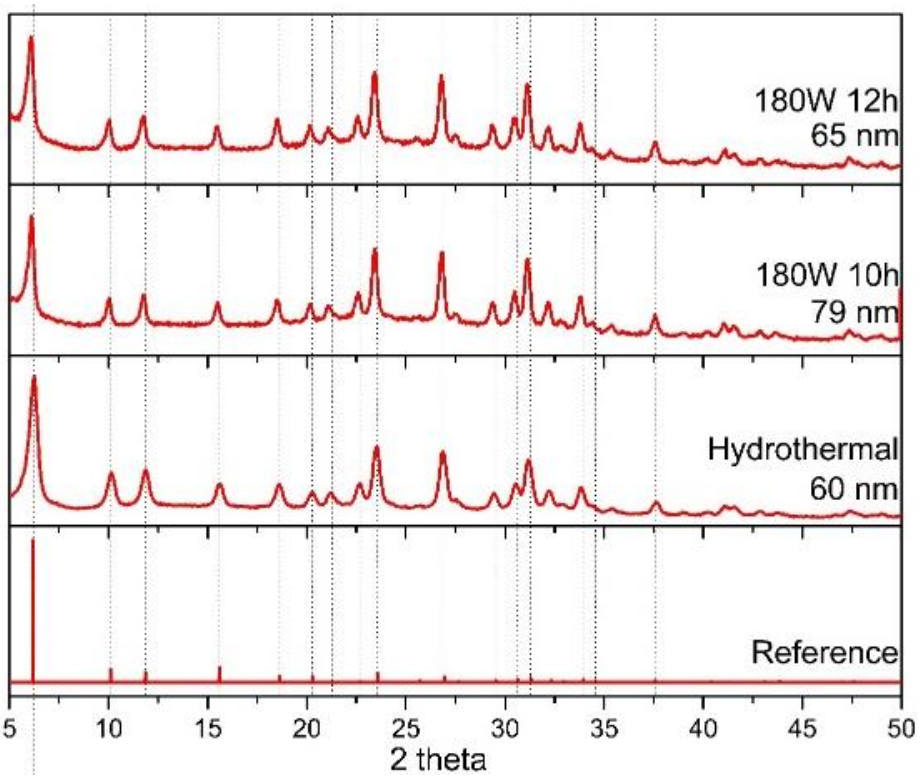

Fig.30. XRD patterns for 180 W

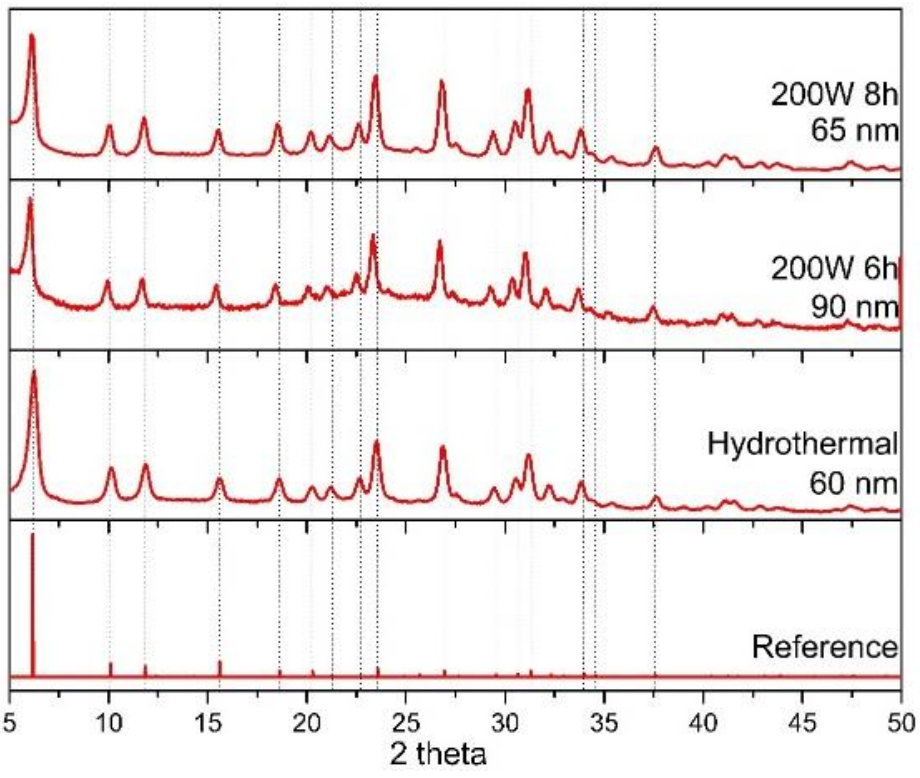

Fig.31. XRD patterns for 200 W

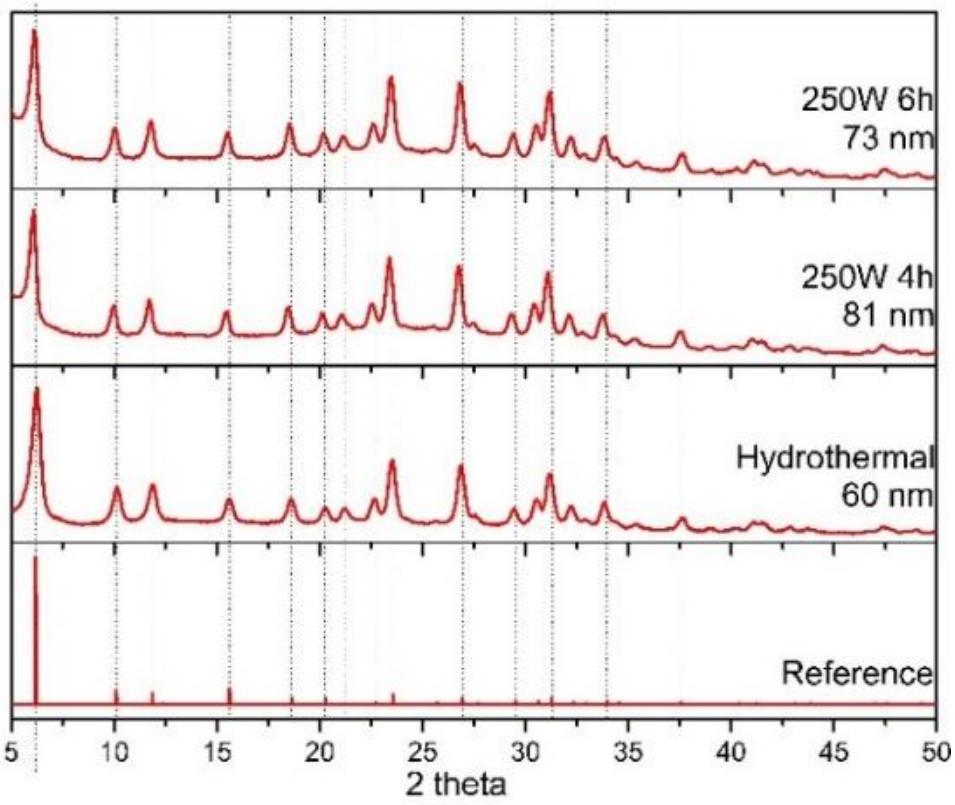

Fig.32. XRD patterns for 250 W

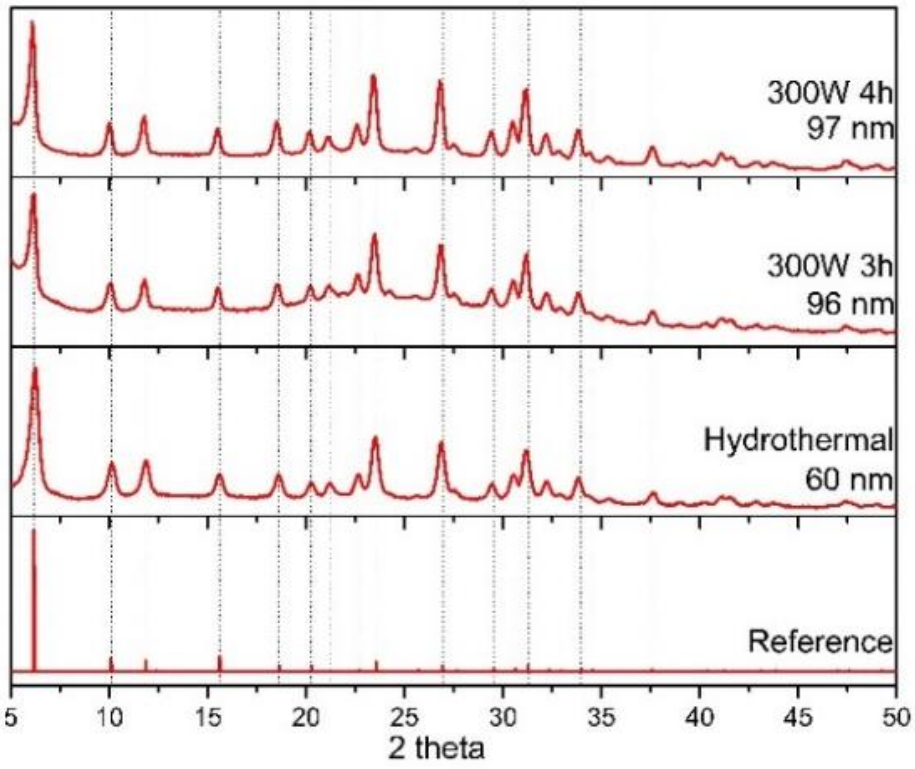

Fig.33. XRD patterns for 300 W

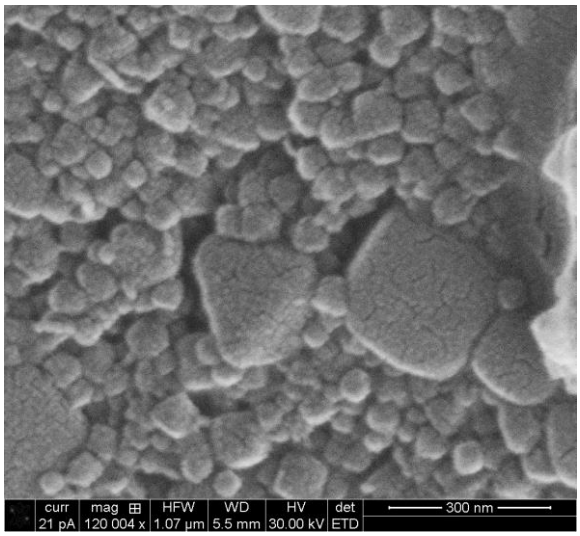

Fig. 34. SEM of Microwave Synthesized Raw Nano Zeolite Y with 200W for 8 hours

Although the yield of microwave synthesis is higher than hydrothermal synthesis, the overall yield is still very low. According to Song's work[50], the clear synthesis solutions (mother solution) after removing zeolite nanocrystals can be reused, which can produce significantly higher product yield for nanocrystalline Y zeolite. This method is examined by using microwave synthesis. Pure mother solution of hydrothermally synthesized zeolite Y has been mixed with 0.015 g of NaOH and microwave synthesized at 200W for 3 hours. The zeolite crystal size and the results are listed in Table 4. The representative XRD pattern for eighth batch is shown in Fig. 32.

	Gel #1		Gel #2		Gel #3	
	Size (DLS)	Yield	Size (DLS)	Yield	Size (DLS)	Yield
1st batch (hrdro)	50nm	20mg	50nm	20mg	50nm	20mg
2nd batch (MW)	41.08nm	130mg	40.09nm	130mg	47.4nm	130mg
3rd batch (MW)	39.98nm	130mg	34.76nm	130mg	37.51nm	130mg
4th batch (MW)	40.06nm	130mg	43.47nm	130mg	40.64nm	130mg
5th batch (MW)	41.08nm	130mg	39.09nm	130mg	36.32nm	130mg
6th batch (MW)	39.95nm	130mg	37.90nm	130mg	39.25nm	130mg
7th batch (MW)	44.58nm	130mg	39.24nm	130mg	51.8nm	60mg
8th batch (MW)	51.03nm	100mg	47.06nm	50mg	52.38nm	30mg

Table 6. Microwave Synthesis of nano zeolite Y by using mother solution

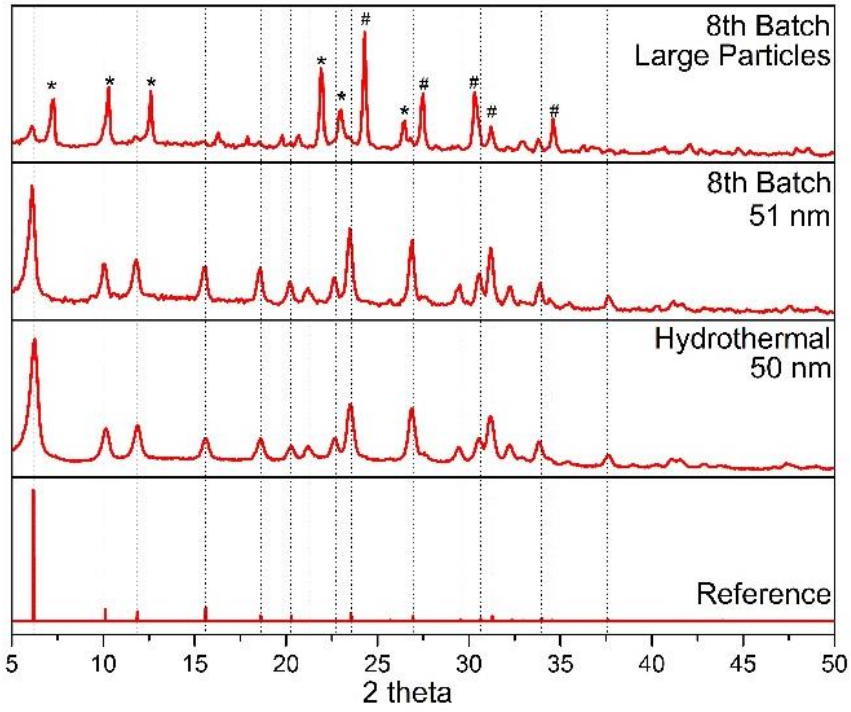

Fig.35. XRD patterns for Batch 8

Starting from the 8th batch, amount of large particles increases from very small amount to the amount enough for making the whole tube turbid. Large particles are mainly zeolite A (*) and sodalite (#). As more batches of recycling goes, yield of small zeolite Y decreases. Small particles are still pure zeolite Y. Total yield of small zeolite Y of the 10 batches of recycling synthesis is around 70%, which is higher than the reported hydrothermal recycling method (~43%). The reason for higher yield and lower crystallization time by using mother solution as comparing to starting gel still needs further investigation. Our assumption is that the clear synthesis solutions contains large amount of nuclei of zeolite Y.

Microwave synthesis is usually used to improve industrial applications. Microwave heating occurs in a volumetric manner, dielectric substances can be quickly and internally heated[51,52] without requiring heat transfer from the surrounding gas as in thermal swing adsorption processes[53]. Desorption under microwave heating is a rapid and effective way to regenerate

adsorbent beds leading to energy savings in some cases as compared to classical hydrothermal methods[54]. One possible reason of the enhanced rates observed in the microwave syntheses may derive from an acceleration of reagent digestion and aluminosilicate equilibration processes to produce a medium which is more homogeneous on a molecular scale. However, perhaps an even more significant effect may be occurring at crystal surfaces where microwave energisation of the hydroxylated surface or of associated water molecules in the boundary layer may be linked to specific energy dissipation.

The crystallization of zeolite is usually limited by limitations at the nucleation stage. Therefore, it is easy to understand why to age reaction gel or add nucleants to them. It was suggested that the rearrangement of the synthesis mixture to yield nuclei was the bottleneck in a microwave synthesis[55]. Without enough nuclei in the reaction gel, the selectivity and crystallization of zeolite by using microwave synthesis is limited. This can explain why the product of three day aged gel is a mixture of large particles of zeolite A and small particles of zeolite Y. Clear mother solution which has more nuclei of zeolite Y can produce higher yield and better selectivity. The crystallization time is seven times shorter than microwave radiation synthesis of three days aging gel. Only a small amount of zeolite A presents in the final product. Therefore, our assumption of large amount nuclei of zeolite Y in the mother solution can be plausible.

4. Conclusion

Dehydration-hydration process for rapid synthesis for ZSM-5 and Mazzite is developed. This rapid synthesis method emphasizes the role of [OH^-] in morphological and chemical transformation. Dense populations of viable nuclei can rapidly crystalize with the addition of

water. The organic template used in synthesizing mazzite is proven to exhibits a good structure directing capability both for gmelinite and sodalite cages. Therefore, there is a competitive forming process between mazzite and sodilate. As stated in our results, with high alkalinity, the crystallization rate of sodilate is higher than mazzite. Compared with mazzite synthesis, the synthesis of ZSM-5 does not have this problem. The organic template TPA^+ is so good that there is only one kind of cage than can be directed. Therefore, this procedure may not be able to be generally used by other frameworks since during most synthesis there will be more than one cage presented in the concentrated gel.

The crystal sizes of nanocrystalline Y zeolites synthesized using recycled clear synthesis solutions are uniform and the Si/Al ratios of different batches are constant. Nanocrystalline zeolite Y with high quality can be synthesized more efficiently and rapidly. From an environmental perspective, this procedure is extremely beneficial that the waste can be minimized by reusing the starting materials.

Further studies

For the next phase for rapid synthesis of mazzite, we will only focus on one cycle, as shown in Figure 33. The reaction will be continued for two hours. Then, evaporated water will be collected by the constant pressure drop funnel for thirty minutes. 20 mL of water (14% of water in the reaction) will be collected. After ten hours' reaction, water will be dropped back in thirty minutes. 5 mL of dioxane will be added into the concentrated gel right after the water is extracted. Timeline is shown in Figure11. Also, the mechanism of rapid microwave synthesis will be studied. Terbium ions can be stuck in the cages of zeolite Y. A strong peak for terbium can be detected by fluorescence spectroscopy. If there is a large amount of nuclei of zeolite Y, the terbium in the cage

should be detected. This method can help us test our assumptions.

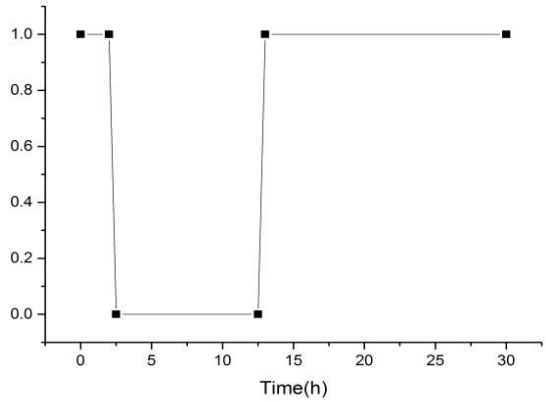

Fig.36. Timeline of reaction for mazzite

Reference

1. R. J. Argauer and G. R. Landolt, “Crystalline Zeolite ZSM-5 and Method of Preparing the Same”; US Pat. 3702886, 1972.
2. G. T. Kokotailo, S. L. Lawton, D. H. Olson, and W. M. Meier, “Structure of Synthetic Zeolite ZSM-5,”Nature, 272, 437–8 (1978).
3. http://www.iki.kfki.hu/isoappl/research/porous_hu.shtml
4. J. W. JUN, I. Ahmed, C. Kim, K. Jeong, S. Jeong, S. H. Jhung. Synthesis of ZSM-5 zeolites using hexamethylene imine as a template: Effect of microwave aging. Catalysis Today, 2014, 232, 108-113.
5. M. K. Naskar, D. Kundu, M. Chatterjee. Synthesis of ZSM-5 Zeolite Particles Using Triethanol Amine as Structure-Directing Agent. J. Am. Ceram. Soc., 2012, 95[2] 449–452.
6. N. Y, KangBu, S. Song, C. W. Lee, W. C. Choi, K. B. Yoon, Y. Park. The effect of Na_2SO_4 salt

on the synthesis of ZSM-5 by template free crystallization method. Microporous and Mesoporous Materials, 2009, 118, 361-372.

7. P. Wang, B. Sheng, J. Gao. Synthesis of ZSM-5 zeolite from expanded perlite and its catalytic performance in FCC gasoline aromatization. Catalysis Today, 2007, 125, 155-162.
8. M. Ghiacia, F. Seyedeyn-Azad, R. Kia. Fast and efficient synthesis of ZSM-5 in a broad range of SiO2/Al2O3 without using seeding gel. Materials Research Bulletin, 2004, 39, 1257-1264.
9. O. G. Somani, A. L. Choudhari, B. S. Rao, S. P. Mirajkar. Enhancement of crystallization rate by microwave radiation: synthesis of ZSM-5. Materials Chemistry and Physics, 2003, 82, 538-545.
10. S.J. Kulkarni, P. Srinivasu, N. Narender, K.V. Raghavan. Fast and efficient synthesis of ZSM-5 under high pressure. Catalysis Communications, 2002, 3, 113-117.
11. H. Zhu, Z. Liu, D. Kong, Y. Wang, X. Yuan, Z. Xie. Synthesis of ZSM-5 with intracrystal or intercrystal mesopores by polyvinyl butyral templating method. Journal of Colloid and Interface Science, 2009, 331, 432-438.
12. B. Kalita, A. K. Talukdar. An efficient synthesis of nanocrystalline MFI zeolite using different silica sources: A green approach. Materials Research Bulletin, 2009, 44, 254-258.
13. R. Anuwattana, K. J. Balkus Jr, S. Asavapisit, P. Khummongkol. Conventional and microwave hydrothermal synthesis of zeolite ZSM-5 from the cupola slag. Microporous and Mesoporous Materials, 2008, 111, 260-266.
14. A.J. Perrotta, C. Kirby, B.R. Mitchell, E.R. Tucci, J.Catal. 55 (1978) 240.
15. J.F. Cole, H.W. Kouwenhoven, in: W.M. Meier, J.B.Uytterhoeven (Eds.), Molecular Sieves, ACS Symposium, vol. 121, American Chemical Society, Washington DC,1973, p. 583
16. E.M. Flanigen, E.R. Kellberg, US Pat. 4, 241 (1980) 036
17. E. Bowes, J.J. Wise, US Patent 3, 578 (1971) 728
18. V. Solinas, R. Monaci, B. Marongiu, L. Forni, Appl. Catal. 5 (1983) 171.
19. F. Fajula, R. Ibarra, F. Figueras, C. Gueguen, J. Catal. 89 (1984) 64.
20. F. Raatz, C. Travers, C. Marcilly, T. Des Couri_eres, F. Fajula, F. Figueras, US Pat. 5, 157(1991) 198.
21. Sofia Calero, Merijn Schenk, David Dubbeldam, Theo L.M. Maesen, Berend Smit, Journal of Catalysis, 228 (2004) 121-129

22. Di Renzo, Francesco; Fajula, Francois; Fitoussi, Fredj; Schulz, Philippe From PCT Int. Appl. (1997), WO 9746487 A2 19971211
23. http://www.iza-online.org/natural/Datasheets/Mazzite/mazzite.htm
24. A.M. Goossens, J.P Eddy. G. Verhoeven, B.H. Wouters, P.J. Grobet, P.A. Jacobs, J.A. Martens, Microporous and Mesoporous Materials 35–36 (2000) 555–572
25. H. Xu, P. Dong, L. Liu, J.-G. Wang, F. Deng, J.-X. Dong, J Porous Mater (2007) 14:97–101,DOI 10.1007/s10934-006-9013-2
26. Christine Bebon, Didier Colson, B. Marrot, J. P. Klein, F. D. Renzo, Microporous and Mesoporous Materials 53 (2002) 13–20
27. M.A. Zanjanchi, A. Razavi, Spectrochimica Acta Part A 57 (2001) 119–127
28. **B.** De Witte, J. Patarin, J.L. Guth, T. Cholley, Microporous Materials 10 (1997) 247-257
29. D. Barthomeuf, Basic zeolites: characterization and uses in adsorption and catalysis, Catalysis Reviews—Science and Engineering 38 (4) (1996) 521–612.
30. J. Weitkamp, U. Weiss, S. Ernst, New aspects and trends in zeolite catalysis, Studies in Surface Science and Catalysis 94 (1995) 363–380.
31. P.G. Smirniotis, L. Davydov, E. Ruckenstein, Composite zeolite-based catalysts and sorbents, Catalysis Reviews— Science and Engineering 41 (1) (1999) 43–113.
32. L.M. Huang, Z.B. Wang, J.Y. Sun, L. Miao, Q.Z. Li, Y. Yan, D.Y. Zhao, Fabrication of ordered porous structures by self-assembly of zeolite nanocrystals, Journal of the American Chemical Society 122 (14) (2000) 3530–3531
33. L.D.Rollmann et al, Inorg.Syn. 1983,22,67
34. H. Robisin, K.P. Lillerud, Verified Synthesis of Zeolitic Materials (2001) 193-195
35. B. A. Holmberg, H. Wang, J. M. Norbeck, Y. Yan, Microporous and mesoporous Materials 59(2003) 13-28
36. Harris, J.C. Powder X-ray Diffraction https://carmenwiki.osu.edu/display/10137/XRD
37. Marcotolo, http://en.wikipedia.org/wiki/Scanning_electron_microscope
38. Adenosine, http://en.wikipedia.org/wiki/Dynamic_light_scattering
39. M.M.J.Treacy,J.B.Higgins, Collection of Simulated XRD Powder Patterns for Zeolites (2001),7.94
40. M. Severance, B. Wang, K. Ramasubramanian, L, Zhao, W.S. Winston Ho, P.K. Dutta,

Langmuir 2014, 30, 6929-6937

41. J.Warzywoda, R.W.Thompson, Zeolite 9 (1989) 341
42. R.W.Thompson, A.Dyer, Zeolite 5 (1985) 292
43. Flanigen, E. M.; Breck, D. W.137th Meet, ACS, Div. Inorg. Chem. 1960, 33-M
44. Chang, C. D.; Bell, A. T.Catal. Lett. 1991, 8, 305
45. M.M.J.Treacy,J.B.Higgins, Collection of Simulated XRD Powder Patterns for Zeolites (2001),5.55
46. M.M.J.Treacy,J.B.Higgins, Collection of Simulated XRD Powder Patterns for Zeolites (2001),14.16
47. Burkett, S. L.; Davis, M. E.J. Phys. Chem. 1994, 98, 4647.
48. P.D. Hopkins, in M.L. Occelli and H.E. Robson (Eds), Zeolite synthesis, ACS Symposium Series, 398, 1989. p. 152.
49. B. De Witte, J. Patarin, J.L. Guth, T. Cholley, Microporous Materials 10 (1997) 247-257
50. W. Song, V. H. Grassian and S. C. Larsen, Chem Commun, 2005,2951-2953
51. Thostenson, E.; Chou, T. Microwave processing: fundamentals and applications.Composites, Part A1999, 30, 1055–1071.
52. Roussy, G.; Pearce, A.Foundations and Industrial Applications of Microwaves and Radio Frequency Fields Physical and Chemical Processes; Wiley: New York, 1995.
53. Polaert, I.; Ledoux, A.; Estel, L.; Huyghe, R.; Thomas, M. Adsorbents regeneration under microwave irradiation for dehydration and volatile organic compounds gas treatment.Int. J. Chem. React. Eng. 2007, 5, 941–948.
54. Kao, K. C.Dielectric Phenomena in Solids with Emphasis on Physical Concepts of Electronic Processes; Elsevier Academic Press, San Diego, CA, 2004.
55. C. S. Cundy, R. J. Plaisted and J. P. Zhao, Chem. Commun, 1998, 1465-1466